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The Catalytic Power of Portland Cement Gels

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THE CATALYTIC POWER OF PORTLAND CEMENT GELS

by

Constantine Aloysius Neugebauer UC 1953 U C
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A thesis presented to the Department of Chemistry of
Union College in partial fulfillment of the requirements
for the degree of Bachelor of Science in Chemistry.

By Constantine A. Neugebauer

Approved by Charles B. Sturd

May 30, 1953

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This thesis summarizes the research conducted during the period June 1952 - June 1953 under the research fellowship established in the Department of Chemistry at Union College by the North American Cement Corporation.

The research was performed under direction of Professor Charles B. Hurd, to whom the author is much indebted for many helpful suggestions and ideas.

Gift of Author, January 10, 1963

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CONTENTS

Introduction

Preparation of Cement Gel Catalysts

Catalysis and Contact Catalysis

Apparatus and Procedure

Analytical Procedures

Dehydration Reactions

A. The Dehydration of Ethyl Alcohol

B. The Dehydration of Other Alcohols

1. Methyl Alcohol

2. The Propyl Alcohols

3. The Butyl Alcohols

C. The Condensation of Water Between Ethyl Alcohol and Aromatic Compounds

1. Between Ethyl Alcohol and Phenol

2. Between Ethyl Alcohol and Aniline

D. The Dehydration of Ethylene Glycol

E. The Dehydration of Various Other Compounds

1. The Dehydration of Ethyl Ether

2. The Dehydration of Acetone

The Pyrolysis of Hydrocarbon Oils

A. The Pyrolysis of Paraffin Oil

B. The Pyrolysis of Lubricating Oils

Organic Compounds Unaffected by Cement Gel Catalysts

Summary

References

INTRODUCTION

For several years research has been done at Union College investigating the possibility of using Portland Cement as a chemical raw material. Investigations by Clark in 1951 indicated that vigorous reactions take place when Portland cement and strong acids are mixed. This is evident when one considers the composition of a typical Portland cement:

TABLE I: The Composition of Portland Cement.

SiO_2	23.5 %	CaO	64.3 %
Al_2O_3	4.6 %	MgO	2.02%
Fe_2O_3	3.4 %	SO_3	1.33%

If sufficient acid is added to cement, the calcium and magnesium oxides will all dissolve, and also most of the aluminum and ferric oxides. The silica remains undissolved, unless hydrofluoric acid is used. Also, since the calcium and magnesium oxides are much more basic than the aluminum and ferric oxides, they react with the acid first, and only after most of the oxides have been removed is it possible for the aluminum and ferric oxides to be neutralized, provided there is acid still left over. From these considerations it can be concluded that by very carefully varying the amount of acid used per gram of cement it is possible to remove almost all of the strong oxides and almost none of the weak ones, or, with a somewhat higher ratio of acid to cement, to remove all of the strong oxides and most of the weak ones. The oxides are removed by solution in acid and consequent filtering and washing.

The insoluble reaction products which remain in the filtercake, obtained in the form of gels, vary in composition according to the acid / cement ratio.

To illustrate this, the table below gives the composition of five gels prepared by reacting 1500.0 cc of x normal hydrochloric acid with 150.00 g of Catskill regular Portland cement:

TABLE II: Composition of Cement Gels for Different Concentrations.

<u>Oxide</u>	<u>3.00N</u>	<u>2.75N</u>	<u>2.51N</u>	<u>2.25N</u>	<u>2.00N</u>
SiO ₂	92.30%	89.12%	61.60%	58.78%	55.66%
Al ₂ O ₃	0.62	1.05	3.88	9.91	9.50
Fe ₂ O ₃	0.81	0.23	9.38	8.83	7.20
CaO	3.54 ^W	0.10	1.67	4.82	14.88
MgO	0.25	0.34	0.15	0.18	0.89
Ign. Loss	<u>2.41</u>	<u>8.87</u>	<u>19.20</u>	<u>16.20</u>	<u>11.60</u>
Total	99.30%	99.71%	95.88%	98.73%	99.73%

The analysis for these samples has been done at the laboratories of the Catskill Plant of the North-American Cement Company.

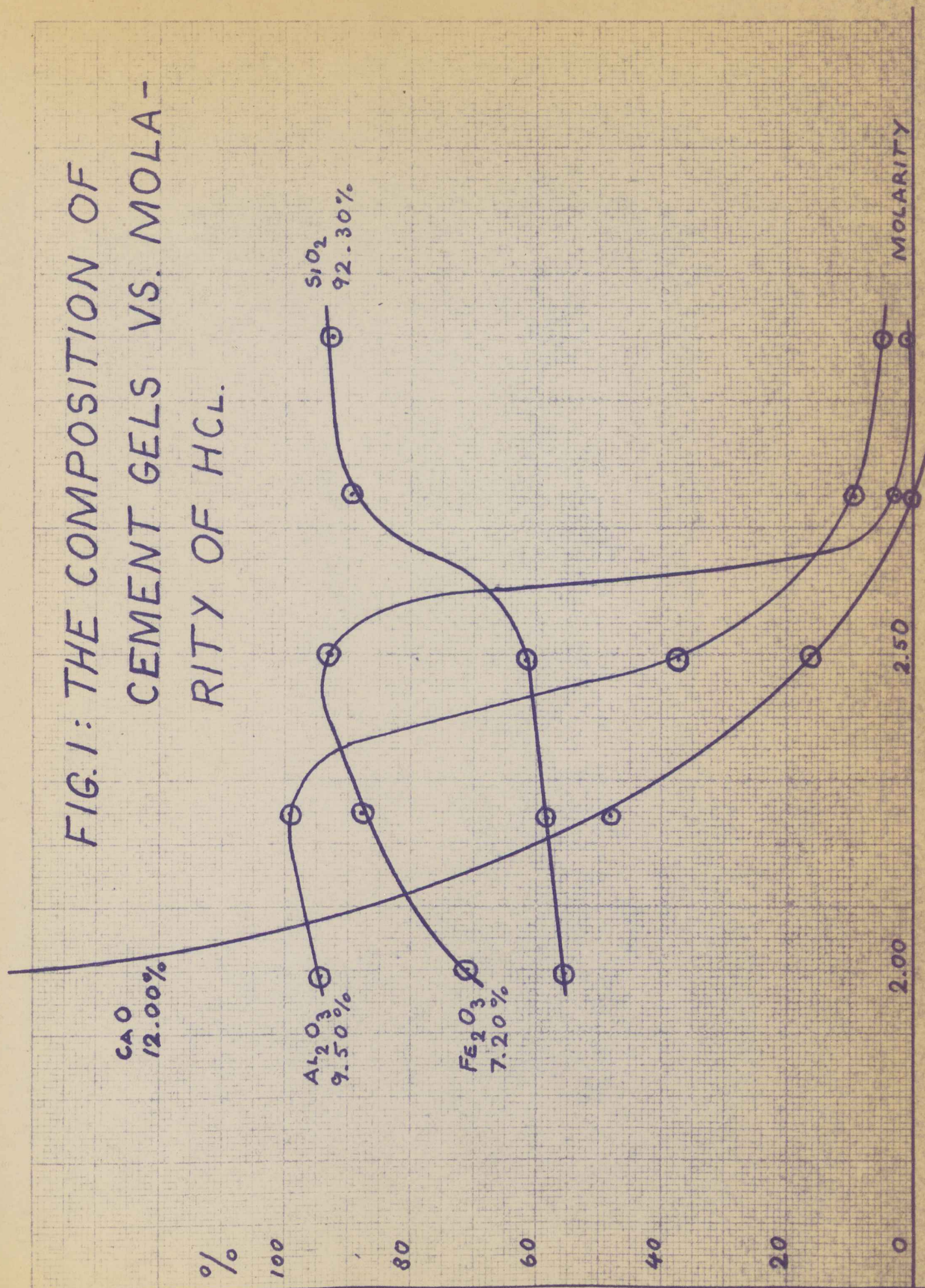
The variation of composition with the concentration of hydrochloric acid is still better seen from the following graph (Figure I), where acid concentration is plotted against percent by weight of the various oxides, according to the data given above.

It can easily be seen how with increasing acid strength the CaO is removed first, then the Al₂O₃, and finally the Fe₂O₃. The SiO₂ content of the gels increases since this oxide is not attacked by hydrochloric acid and the other oxides are removed.

These gels were first investigated by Laudise (8), who prepared them using varying concentrations of hydrochloric, sulfuric, and acetic acid per unit weight of Catskill regular

^W error

FIG. 1: THE COMPOSITION OF
CEMENT GELS VS. MOLARITY
OF HCL.



Portland cement, and investigated the physical properties of the reaction products and their adsorption characteristics. (12)

The research problem for this thesis is to investigate these gels prepared by partial or complete reaction of Portland cement with acids as to their catalytic power. A detailed method of preparation of these catalysts follows below.

THE PREPARATION OF CEMENT GEL CATALYSTS

The catalysts used are the insoluble products from the reaction between Portland cement and acids. The method of preparation is described in the thesis of Laudise on Portland cement (9), but since several changes have been introduced, a complete procedure is given here.

In this procedure, 150.00 g of Portland cement are placed in a two liter Florence flask. Deionized water is now added in such quantity that the sum of the volume of the water and the concentrated acid, which is added in the next step, adds up to 1500.0 cc. The amount of water varies with the concentration of acid desired. The cement and the water are now thoroughly mixed and stirred to give a homogeneous slurry. Then the concentrated acid is added, enough to bring the volume of liquid added to the cement up to 1500.0 cc. Thus the resulting molarity of acid at the moment of mixing is

$$\frac{\text{No. of cc of acid added}}{1500.00} \times \text{molarity of conc. acid}$$

The reaction flask is thoroughly shaken to insure adequate mixing of the acid and the cement, then fitted with a reflux condenser, and digested over a Meker burner for two hours. After this step the mixture is poured into a 20 cm dia Büchner funnel using a towel cloth as a filter instead of filterpaper. The funnel is connected to the suction pump and the reaction products are filtered hot. About 2 minutes are necessary for such a filtration. The residue is washed five times with hot, deionized water, using one liter portions. Hot water keeps the gelatinous products in suspension better and thus has a greater washing power than cold water.

The insoluble reaction product, which is a gel, is now scraped from the filter cloth and dried in an evaporating dish at 125°C. The drying time necessary varies with the gel,

usually about 5 to 8 hours are required. After this drying step the gel is broken up into coarse particles, and is ready for use. Yields of about 40 to 50 g are obtained, depending on the normality of the acid used.

Laudise described in his thesis a washing with dilute sodium hydroxide which is applied to the gels after the drying step (10). However, tests on the catalytic power of gels thus treated revealed a sharp decrease in activity, and this washing is therefore omitted on all gels prepared for catalytic use. In addition, instead of grinding the gel into a fine powder, as Laudise's directions call for, the particle size used in catalytic experiments is about $1/8$ " on a side.

It is a common phenomenon that some reactions run very slowly or not at all, in spite of a rather large negative value for the free energy change. This is due to the fact that it is necessary for molecules to become activated before they can react. In the chemical kinetic sense one may represent such a reaction by

Reactants (A) ^{slow} activated molecules (B) ^{fast} products (C)

The initial molecules A require the absorption of a definite amount of energy in order to put them in an activated state B from which they can rearrange to give the products C. The heat evolved in the step BC is larger than the heat absorbed in step AB in an exothermic reaction, and smaller in an endothermic reaction. The energy required for the activated state is the chief factor in determining the speed of the reaction. The greater the energy required for activation, the fewer are the molecules possessing this energy; and hence, the slower is the reaction at a given temperature.

Any substance which increases the rate of a chemical reaction without being used up in the reaction is called a catalyst. The catalyst brings about this desired increase in the speed of the reaction by decreasing the heat of activation required. A lower heat of activation gives a more rapid reaction because more molecules have the required amount of energy to react. The higher energy requirement is avoided by some bypass. Usually the bypassing consists in forming a new compound or new configuration with less energy consumption, and then decomposing this intermediate compound in such a way as to regenerate the catalyst. (5)

Contact catalysis deals with the chemistry of reactions at the surfaces or at the interface between two phases. Most contact catalytic processes take place at a solid-fluid interface, and of these the larger portion are at a solid-gas interface. In general, adsorption of one or more of

the reactants is a necessary prerequisite for catalytic change. There are two theories of activation due to adsorption. The first, activation by oriented adsorption, consists in an alteration of the configuration of the adsorbed molecule, or the opening up of primary valence bonds or secondary or residual valence bonds on the surface of the catalyst. Since adsorption in this way does not usually lead to great molecular deformation, the second theory of activation assumes that activation results from suitable multiple adsorption, that is, the independent adsorption of the two ends of a molecule by active points on the catalytic surface. If these points are farther apart than the normal length of the molecule, sufficiently strong adsorption will cause stretching and distortion which are assumed to increase molecular reactivity (21).

These two theories indicate the importance of the catalytic surface. Therefore the method of preparation of the catalyst is important, since it is the mode of preparation which is largely responsible for enabling the surface to adsorb and activate molecules.

It has long been known that silica gel is a good adsorbent for many gases and several solutes from solution. This has been shown to be true for cement gels also by Laudise's research last year, where he demonstrated the high adsorbing power of these gels for methylene blue and safranin red.

The adsorption of gases on the solid is essential in contact catalysis, and since gels of the silica-aluminum type do exhibit high adsorption in this respect, it seemed most promising to investigate the catalytic power of the cement gels by making use of this property in contact catalysis. Vapor phase catalysis is exclusively used, that is, the reagent is vaporized before it comes into contact with the cement gel catalyst.

APPARATUS AND PROCEDURE

The apparatus used for vapor phase catalysis consists of essentially 6 parts. The first is the reaction chamber, a thick pyrex glass tube 56 cm long and 2.15 cm inside diameter. This tube is enclosed by an electric muffle oven, whose heating section is 28 cm long. The reaction tube which protrudes 12 cm from the top and bottom of the muffle heater, is fitted on the upper end with a two-hole rubber stopper containing a 60 cc dropping funnel and a one cm thick pyrex tube which is 28 cm long and sealed on that end which is inside the reaction tube. This sealed end will be exactly in the middle of the heating section of the muffle oven, and temperature readings in that oven can be obtained by inserting a chromel-alumel thermocouple into this tubing. The dropping funnel, during a run, is filled with the reagent under investigation, and, by controlling the setting of the stopcock, the liquid can be dropped on the catalyst at the desired rate.

The catalyst is held in a section 10 cm long by two glass wool plugs, one on each end of the section. The glass tube containing the thermocouple extends 5 cm into this catalyst section which is exactly in the middle of the oven. To keep the catalyst from slipping down during a run, the lower glass wool plug is supported by a glass rod, which in turn rests on a one hole rubber stopper fitted on the lower end of the reaction chamber. This stopper contains a glass tube bent to a S shape. This glass tube leads to a two-neck 500 cc round bottom flask, fitted with a reflux condenser. Liquid reaction products are collected here. The condenser, in turn, is connected by means of glass tubing to a manometer, consisting of a U tube half filled with mercury. The manometer on its part is connected by means of rubber tubing to a 5 gallon water bottle which is inverted and rests in a water trough. The neck of this bottle is fitted with a

two hole rubber stopper. Through one hole leads a long glass tubing which touches the upper part of the container, while the other hole is simply fitted with a short piece of glass tubing, extending into the bottle not more than 2 cm. The lower ends of both pieces of tubing are submerged below the water level in the trough. The flask may be filled with water by simply connecting the faucet with the smaller glass tubing with a piece of rubber hose. Water thus enters the bottle on the bottom, while the air is forced out through the long glass tubing on the top. The flask is filled as soon as the water level reaches the height of this tubing. The rubber hose coming from the faucet is now disconnected from the shorter glass tubing, and the rubber tubing coming from the catalytic apparatus is connected to the long glass tubing. Consequently, any gas generated in the catalysis enters the water bottle through the small glass tubing. The pressure on the gas collected in such a manner is below atmospheric pressure by the height of the water level in the flask above the one in the trough. This has to be taken into account in addition to the vapor pressure of water and the temperature when the volume of the gas is measured. The entire apparatus has to be gas-tight.

Immediately before use the catalyst is activated by ignition in an evaporating dish for at least 15 minutes. Since during a run carbon is often deposited on the catalyst, it is also ignited after the run to regenerate the catalyst.

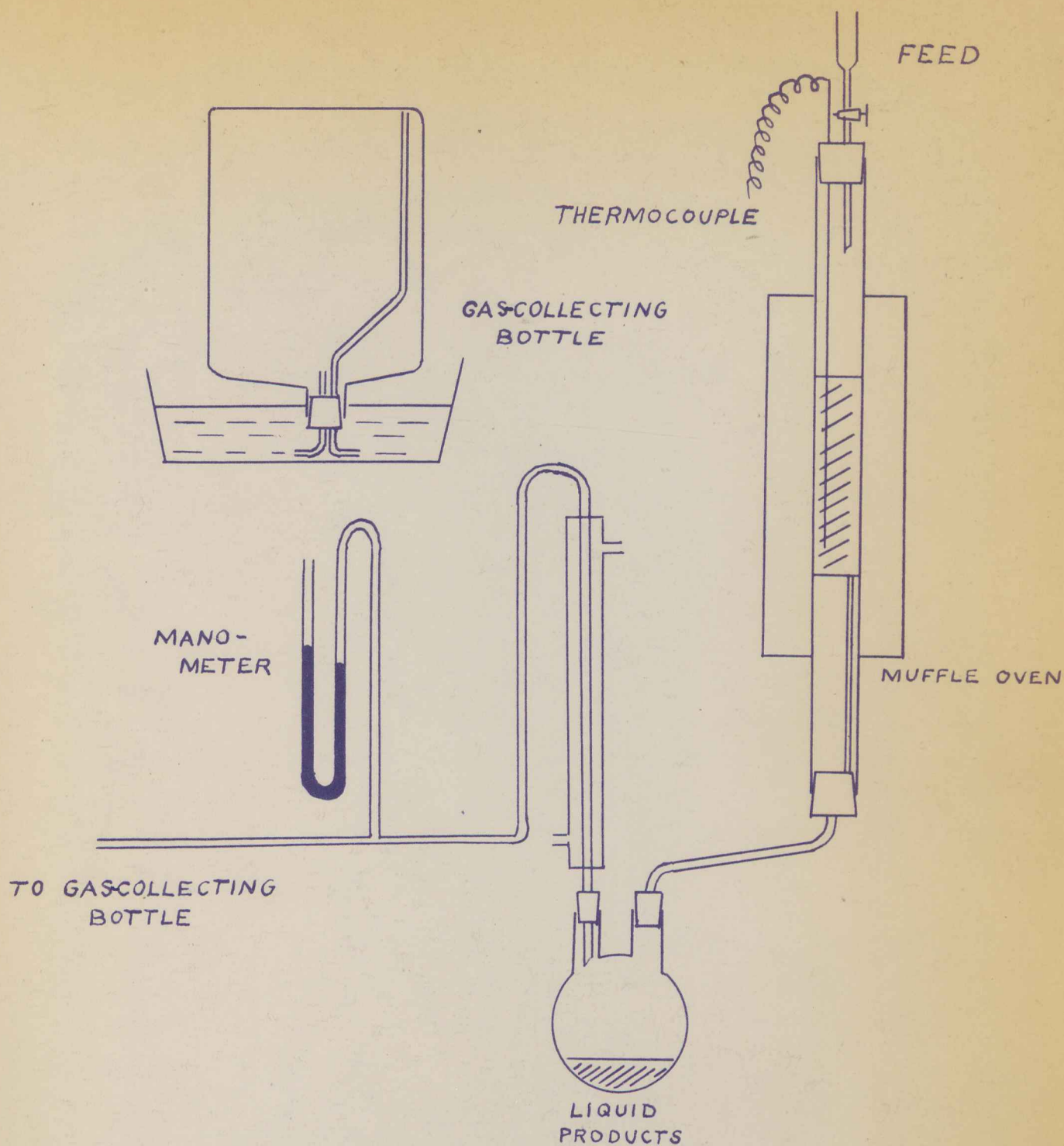


FIGURE II: THE APPARATUS

ANALYTICAL PROCEDURES

The gas collected in the water bottle described above is analyzed in the following manner. An aliquot portion of 2 liters of gas is transferred to a smaller bottle which, except for its size, is identical to the gas collecting bottle described above. The gas transfer is easily effected by connecting the two long glass tubes in each gas bottle with rubber tubing and forcing water into the short glass tubing of the large gas collecting bottle. A Milligan bottle containing a glass spiral is now connected between the bottle containing the aliquot and a third, small gas collecting bottle filled with water. When the gas from the aliquot is forced into the Milligan bottle, the gas bubbles are forced around the spiral and thus remain in contact with the liquid in the Milligan bottle for a relatively long time. By choosing the appropriate liquid or solution in the Milligan bottle, corresponding gases in the aliquot are removed by this treatment, and the volume of gas removed in this manner can be read from the gas collecting bottles, which have been previously calibrated.

The solutions in the Milligan bottle have to be so chosen that the corresponding gases form non-volatile compounds when they are bubbled through it. The following solutions are used:

To remove unsaturated hydrocarbon gases: A 10% solution of bromine in carbon tetrachloride.

To remove oxygen: A concentrated solution of potassium pyrogallate.

To remove carbon dioxide: A concentrated solution of sodium hydroxide.

To remove carbon monoxide: A 5% solution of cuprous chloride. (16)

To analyze for hydrogen, the gas is passed over hot

copper oxide in a pyrex tube. The decrease in volume of gas indicates the quantity of hydrogen present. This procedure is unsatisfactory if saturated hydrocarbon gases are present, which would react with the copper oxide to form carbon dioxide and water. In such a case the gas is passed through the sodium hydroxide solution after the copper oxide treatment.

At least two passes are made through the solutions.

The liquid collected in the two neck flask during the run may be identified by its boiling point in the case of a pure liquid, or, where a mixture of compounds is involved, the products are separated with a fractionating column.

DEHYDRATION REACTIONS

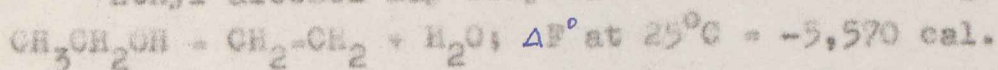
The work on catalysis in this research falls into roughly two groups: Dehydration reactions and the pyrolysis of hydrocarbon oils. The dehydration reactions are given below.

A. The Dehydration of Ethyl Alcohol.

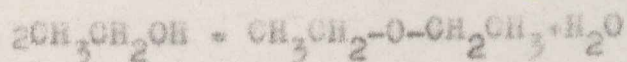
Ipatieff (4) in 1903 found that aluminum oxide, precipitated from aluminum salt solution with bases and then carefully washed to remove all alkali, dehydrates ethyl alcohol to ethylene at 380 - 400°C to an extent of 90%. Other catalysts which have since been used for the same reaction are ThO_2 , WO_3 , ZnO , mixtures of Al_2O_3 , CuO , Ag_2O , NiO , CuSO_4 , Cr_2O_3 , K_2CO_3 , $\text{Mg}_3(\text{PO}_4)_2$, and by metallic calcium.

Since the cement acid gels contain alumina and ferric oxide, they were first tested as to their ability to dehydrate alcohol. Due to the simplicity of the reaction and the products, this reaction turned out to be a very convenient one for testing the relative dehydration capabilities of the various gels.

Ethyl alcohol may dehydrate in the following way:



$$\Delta F^\circ \text{ at } 400^\circ\text{C} = -13,373 \text{ cal. (13)}$$



The first reaction is the one which takes place to a predominant extent with the cement gel catalysts at 400°C. Dried gels are placed in the catalyst tube as described in the section on "Apparatus and Procedure". The total volume of loosely packed gel thus used as a catalyst is 36 cc. The temperature of the catalyst is brought up to $400 \pm 10^\circ\text{C}$ and 30.0 cc of 95% ethyl alcohol are dropped on the catalyst from the dropping funnel within 40 minutes. Thus the contact

time of the alcohol with the catalyst is 1.20 min./cc of alcohol. Since 30 cc of 95% ethyl alcohol correspond to 0.486 moles or 26.9 liters of gas at 400°C , each molecule of alcohol is, on the average, a total of 0.00134 min. or 0.0805 sec. in direct contact with the catalyst in the reaction chamber. The ethylene evolved is collected in the gas collecting bottle and analyzed. At the end of each run 2.0 liters of air are passed through the catalyst chamber to displace all the ethylene still left there. The liquid products, water and unreacted alcohol, are collected in the two-neck flask. Table III below gives the yields of ethylene obtained by this method, using catalysts made by the reaction of Catskill regular Portland cement with hydrochloric and acetic acid of various concentrations.

TABLE III: Yield of Ethylene for Various Catalysts

<u>Acid</u>	<u>Normality of Acid</u>	<u>Yield of Ethylene</u>
HCl	1.00	1%
	2.00	19
	2.15	40
	2.20	72
	2.25	83
	2.30	96
	2.35	99
	2.41	88
	2.46	89
	2.51	86
	2.55	85
	2.60	95
	2.65	84
	2.70	83
	2.75	60
	2.85	22
	3.00	10

<u>Acid</u>	<u>Normality of Acid</u>	<u>Yield of Ethylene</u>
HAc	1.0	1%
	2.0	21
	3.0	40
	4.0	67
	6.0	94
	8.0	89
	12.0	86
	16.0	90

Several gels have been prepared with special clinkers and acetic acid. Yields of ethylene are given below:

TABLE IV: Yield of Ethylene for Various Catalysts.

<u>Normality of Acid</u>	<u>Clinker</u>	<u>Yield of Ethylene</u>
3.0	no gypsum, surface area = 1900	61%
12.0	"	97
3.0	no gypsum, surface area = 950	74
12.0	"	95

It was not possible to prepare gel catalysts with ground high silica limestone rock. The relations of acid concentration against yield of ethylene are given in figures III and IV.

Discussion of the Dehydration of Ethyl Alcohol: By referring to fig. III it can be seen that, in the case of the hydrochloric acid gels high yields are shown in the molar acid range of 2.2 to 2.7 molar. This runs a little either side of the stoichiometrically equivalent amount of HCl. The gels in this range contain not only SiO_2 , but also Al_2O_3 and Fe_2O_3 . By referring to figure I, the gel prepared from 3.00 M HCl, where low yields are obtained, is nearly pure silica. With the 2.75 M HCl gel, showing a yield of 60%,

FIG. III: THE % ETHYLENE VS. MOLARITY
OF HCL.

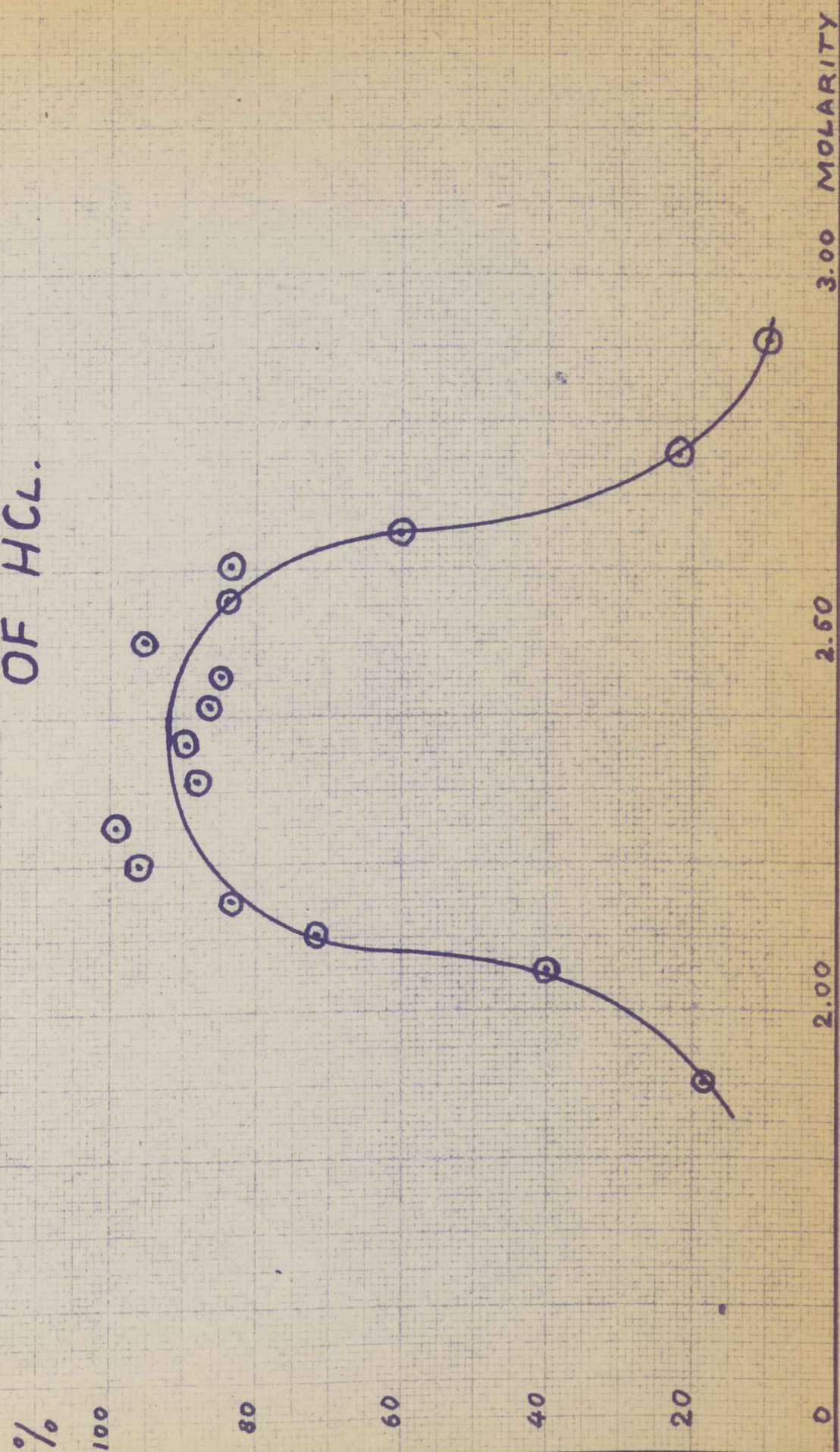
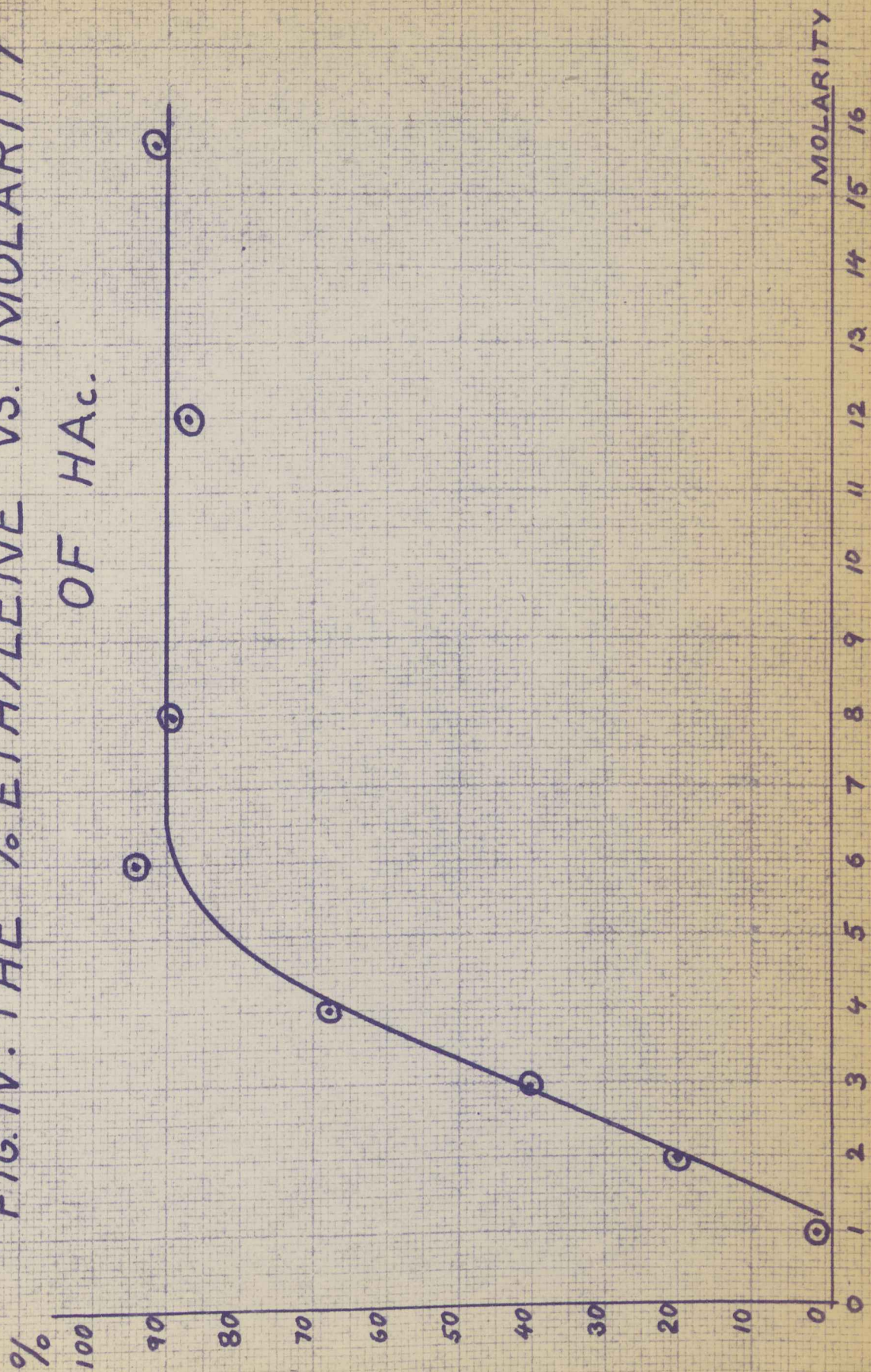


FIG. IV: THE % ETHYLENE VS. MOLARITY
OF HAc .



the Al_2O_3 and Fe_2O_3 have begun to increase. With 2.51M HCl, where yields of about 90% are shown, the Al_2O_3 and Fe_2O_3 contents are quite high, while that of CaO is low. This is due to the fact that the acid dissolves the CaO first, since it is the strongest base forming oxide. The greater part of the Al_2O_3 and Fe_2O_3 are in the gel, giving the best catalyst. The 2.25M HCl gel, still a good catalyst, showing over 80 % yield of ethylene, shows rising content of CaO. The yield drops off fast below 2.25M HCl and the CaO content rises, showing incomplete reaction between cement and HCl.

The conclusion is that the best gels for use as catalysts in the dehydration of ethyl alcohol are those where enough acid has been present to decompose the cement and dissolve most of the CaO, but not enough to dissolve the Al_2O_3 and Fe_2O_3 .

Figure IV shows the relation between the yield of ethylene and the molarity of acetic acid used in preparing the cement gels. Here yields of about 90% of ethylene are shown from the molarity of 6.0 on up. This indicates that acetic acid weaker than 6.0M is not sufficiently strong to dissolve out all of the calcium oxide, which has a poisoning effect. On the other hand, 16M acetic acid, which is extremely concentrated, is not strong enough to dissolve out all of the alumina and ferric oxide, since the yield of ethylene does not decrease for even such a high acid concentration.

The experiments with the special clinker cements indicate that the previous removal of gypsum has no effect on the dehydrating power of the gels.

Materials other than cement gels have also been tried as catalysts for this reaction for purposes of comparison. The apparatus used for these tests is slightly different, the catalyst tube being arranged in a obliqui position instead

of a vertical one. In addition the alcohol is fed into the reaction chamber by vaporization in a boiler. The rate of alcohol feed is somewhat slower, 30.0cc of alcohol per one hour. The temperature is 400°C as before and all other conditions are also the same. The yields for some catalysts are given in table V.

TABLE V: Yields of Ethylene for Various Catalysts.

<u>Catalyst</u>	<u>Yield of Ethylene</u>
Davison Silica gel	40%
Ottawa Sand	0
calcium oxide	0
Monsanto Silica Aero gel	0
Al_2O_3 , sticks	33
Al_2O_3 , curdy	65
Al_2O_3 , modified by Dr. Sheffer, sticks	93

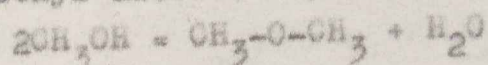
These results indicate that silica alone is not a very efficient catalyst for dehydration reactions of alcohols. In addition it may be noted that the mode of preparation and structure of even an active oxide such as alumina is important in catalytic reactions.

B. Dehydration of Other Alcohols.

Here again the oblique apparatus is used, but this time the electric heater is replaced by a gas oven. This arrangement has been used in the earlier runs. The rate of feed for all the alcohols in this section is 0.25 moles per hour.

1. Methyl Alcohol.

Methyl alcohol may dehydrate in the following manner:



This is the reaction which takes place to the predominant extent. The further dehydration to ethylene



does not take place at all, since in no analysis are unsaturated gases found. The following are some yields of dimethyl ether, obtained by passing methyl alcohol over various Catskill regular cement gels at 400°C (unless given differently):

TABLE VI: Yields of Methyl Ether for Various Catalysts.

<u>Catalyst, Acid Conc.</u>	<u>Yield of Methyl Ether</u>
2.5M HCl	63% (T = 450°C)
4.0M HAc	63 (T = 460°C)
12.0M "	75
16.0M "	75 (T = 460°C)

Analytical Details: The methyl ether is analyzed quantitatively by passing the gas which has not condensed in the condenser fitted two-neck flask through a calcium chloride drying tube to take out the water vapor and then through a flask immersed into an acetone-dry mixture. The yield of methyl ether, which boils at -23.7°C, is obtained by reading the volume of the ether obtained from the graduated dry ice trap. The ether is identified by its boiling point, it has always been found to be within at least 2° of the boiling point of the pure substance.

2. The Propyl Alcohols.

n-propyl alcohol may dehydrate according to the equation



and isopropyl according to the equation



The following are some yields of propylene, obtained by passing propyl alcohol over various Catskill regular cement

gels at 400°C:

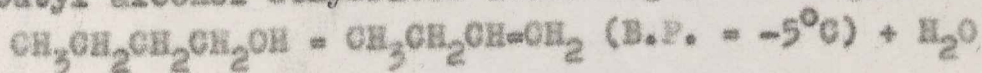
TABLE VII: Yields of Propylene for Various Catalysts

<u>Alcohol</u>	<u>Catalyst, Acid Conc.</u>	<u>Yield of Propylene</u>
n-propyl	2.5M HCl	91%
"	4.0M HAc	98
"	12.0M HAc	92
iso-propyl	2.5M HCl	92
"	4.0M HAc	98
"	12.0M HAc	91

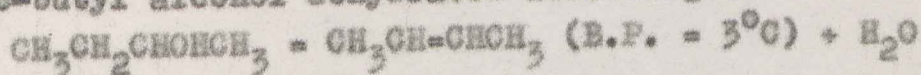
Analytical Details: The propylene is condensed in a dry ice-acetone trap as in the case for methyl alcohol described above. The product is then identified by its boiling point.

3. The Butyl Alcohols.

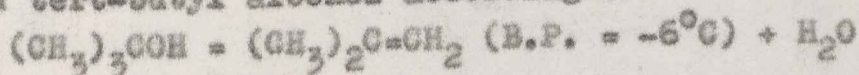
n-butyl alcohol dehydrates according to the equation



sec-butyl alcohol dehydrates according to



and tert-butyl alcohol according to



The following are some yields of butylene, obtained by passing butyl alcohol over various Catskill regular cement gels at 400°C:

TABLE VIII: Yields of Butylene for Various Catalysts.

<u>Alcohol</u>	<u>Catalyst, Acid Conc.</u>	<u>Yield of Butylene</u>
n-butyl	2.5M HCl	95%
"	12.0M HAc	95
sec-butyl	4.0M HAc	98
"	12.0M HAc	95

<u>Alcohol</u>	<u>Catalyst, Acid Conc.</u>	<u>Yield of Butylene</u>
tert-butyl	2.5M HCl	95%
"	12.0M HAc	93

Analytical Details: The butylene is condensed in a dry ice trap and identified by its boiling point as described above.

Conclusion: Alcohols higher than ethyl alcohol all show yields above 90% dehydration, regardless of the cement gel catalyst used. It is therefore easier to dehydrate higher alcohols with these catalysts.

C. The Condensation of Water Between Ethyl Alcohol And Aromatic Compounds.

1. Between Ethyl Alcohol and Phenol

Water may be condensed between ethyl alcohol and phenol in the following ways:



Di-, and possibly tri-substitution also occurs. Ethylene resulting from the dehydration of ethyl alcohol is an inevitable byproduct. No diphenyl ether is produced by the splitting out of water between two molecules of phenol.

In the first run a solution of 1.00 mole of phenol in 1.05 moles of 95% ethyl alcohol, giving a total of 150 cc, is passed over the 16.0M HAc Catskill regular cement gel at 350°C at a rate of 50 cc / hour. The oblique position of the catalyst chamber is used in this and the following run. However, the boiler is replaced by a dropping funnel feed. The analysis of the yield is as follows:

unchanged phenol	59% (B.P. = 184-200°C)
ethyl phenols	16 (B.P. = 200-250°C)
phenyl ethers	3 (B.P. = 172-250°C)
ethylene	36

In the second run a solution of 0.96 moles of phenol in 2.00 moles of 95% ethyl alcohol, giving a total of 200 cc, is passed over the 16.0M HAc Catskill regular cement gel at 400°C at the rate of 50 cc / hour. The analysis of the yield is as follows:

unchanged phenol	36%
ethyl phenols	38
phenyl ethers	1
ethylene	51

By comparing the two runs it can be concluded that by doubling the ratio of alcohol to phenol and increasing the reaction temperature 50°C, the yield of substituted phenols can be more than doubled.

Analytical Details: The liquid products collected in the condenser-fitted flask are made strongly alkaline with 20% NaOH, giving water soluble sodium phenoxides. The phenyl-ethyl ethers do not react with the base and can be extracted with ethyl ether, which is subsequently removed by distillation. After the removal of the ethyl ether the liquid is distilled in an ordinary distilling flask. The range boiling from 172-250°C is taken as containing phenyl ethers.

The remaining alkaline layer of sodium phenoxides is neutralized with excess hydrochloric acid and the phenols are separated with a separatory funnel. The water layer is washed several times with benzene, which is added to the phenol layer. The benzene is now distilled off and the rest

of the liquid is fractionated in a distilling column. Everything boiling from 200-250°C is taken as ethyl phenols. The percentage given for the phenols is based on the original quantity of phenol put through the catalyst, while the percentage for ethylene is based on the original quantity of ethyl alcohol. (15)

2. Between Ethyl Alcohol and Aniline.

Water may be condensed between ethyl alcohol and aniline in the following ways:



Simultaneous alkylation of the ring and the amino group is also possible. Ethylene is formed due to the dehydration of ethyl alcohol.

In the run 0.516 moles of aniline and 0.972 moles of ethyl alcohol, giving a molar ratio of about 1:2, are passed over the 16M HAc Catskill regular cement gel at 400°C at a rate of 50 cc / hour. The normal, vertical position of the catalyst tube is here used, as described in the section on "Apparatus and Procedure". The analysis of the yield is as follows:

unchanged aniline	49%	(B.P. = 187-200°C)
mono substituted aniline	32	(B.P. = 200-220°C)
poly substituted aniline	17	(B.P. = 220-245°C)
ethylene	36	

Analytical Details: The aniline layer is separated by

separatory funnel from the water layer and is then distilled in a fractionating column. The fractions are taken as indicated by the boiling point ranges above. Here again the percent of ethylene is calculated on the basis of the total amount of ethyl alcohol passed through the reaction chamber.

Percentages of both, substituted phenol and aniline, are calculated by estimating their extent of substitution from their boiling point ranges.

D. The Dehydration of Ethylene Glycol.

Ethylene glycol may split out water in the following way:
 $\text{CH}_2\text{OH}-\text{CH}_2\text{OH} = \text{CH}_3\text{CHO} + 2\text{H}_2\text{O}$, acetaldehyde.

This is the primary reaction over the cement gel catalysts. Another possibility is the splitting out of two waters to give acetylene: (2)



50 cc of ethylene glycol are passed over the Catskill regular cement gel catalysts at 400°C at a rate of 50 cc / hour. The normal, vertical position of the catalyst tube is used. The following are the yields of acetaldehyde and unsaturated gas for some of the gels:

TABLE IX: Yields of Acetaldehyde and Unsaturated Gas.

<u>Catalyst</u>	<u>Yield, Acetaldehyde</u>	<u>Yield, Unsat. Gas</u>
acetic acid		
16.0M	53%	1.08 liters
8.0M	41	1.07
6.0M	27	2.30
4.0M	24	2.07

<u>Catalyst</u>	<u>Yield, Acetaldehyde</u>	<u>Yield, Unsat. Gas</u>
Hydrochloric a.		
4.0 N	25%	0.00 liters
2.70N	48	0.59
2.51N	40	1.11
2.25N	44	1.28
2.00N	44	1.28
1.00N	37	1.03
pyrex glass beads	0.2	0.00

Analytical Details: To prevent any acetaldehyde, which is a very volatile liquid, from entering the gas collecting bottle, two ice traps are put between the condenser and the gas collecting bottle. At the end of the run all liquid products are thrown together and that portion of it boiling below 100°C is collected in ice by distillation. An aliquot of exactly 5.00 cc is taken from it and a few particles of anhydrous CaCl_2 are added. The graduate containing the aliquot is then kept in the refrigerator for 24 hours. The water layer has then separated, and the volume of acetaldehyde can be read by differences in level. (1)

The unsaturated gas is analyzed by bromination.

Discussion of Results: The trend shown by the acetic acid cement gels is evident and consistent. The yield of acetaldehyde increases with increasing normality of the acid. In the dehydration of ethyl alcohol yields are about 90% ethylene from the normality of acid of 6.0 on up. In the dehydration of ethylene glycol, however, yields are steadily rising with increase in normality, and the straightening out to a constant yield of acetaldehyde is not so noticeable.

The volume of unsaturated gas, presumably acetylene, reaches a maximum at the 6.0N HAc gel. This gel contains

a considerable amount of Fe_2O_3 , but hardly any CaO .

The trend shown by the hydrochloric acid cement gels is that a yield of about 45% of acetaldehyde is exhibited in the range of acid concentration from 2.00 to 2.70 molar. Yields drop off somewhat on either side of this molarity. However, no sharp changes in yield are noted as in the case of the dehydration of ethyl alcohol, where yields are high in the same general range, but where the yield of ethylene increases from 20 to 80% and drops from 80 to 20% within only about 0.10 normality unit. This would seem to indicate that the chemical composition of the catalysts is not very decisive in the dehydration of ethylene glycol, but that rather the surface properties of the catalysts are largely responsible for it. The maximum for unsaturated gas production falls about at the 2.25M HCl gel.

E. The Dehydration of Various Other Compounds.

1. The Dehydration of Ethyl Ether.

Ethyl ether loses water to form ethylene. 30.0 cc of ethyl ether are passed over the 12.0M HAc Catskill special clinker to which no gypsum has been added and which has a surface area of 1900. The temperature is 400°C and the rate is 60 cc / hour. The regular, vertical position of the catalyst tube is used.

The gas collected is unsaturated and corresponds to 73% yield if the reaction is considered to give only ethylene. However, some butylene-2 is probably also formed, so that the dehydration might be more complete than only 73%.

2. The Dehydration of Acetone.

Acetone dehydrates to give $\text{CH}_2=\text{C}=\text{CH}_2$. In the first run, 43 cc of acetone are passed over the 2.25M HCl Catskill regular cement gel at 400°C in 2 1/2 hours. The oblique

position of the catalyst tube is used, heat being supplied by a gas oven. 0.096 moles of unsaturated gas are formed, amounting to 16% yield if the reaction proceeded in the above sense.

In the second run, 37 cc of acetone are passed over the 12.0M HAc Catskill regular cement gel at 550°C in 2 1/2 hours, using the same apparatus as above. 0.105 moles of unsaturated gas are formed, corresponding to a yield of 21% in the sense of the above reaction.

Some intermolecular dehydration of acetone also occurs, as is evidenced by 0.5 cc and 1.0 cc yields of insoluble oils, respectively.

In general the dehydration of acetone does not go to completion, which is indicated by unreacted acetone recovered from the liquid products.

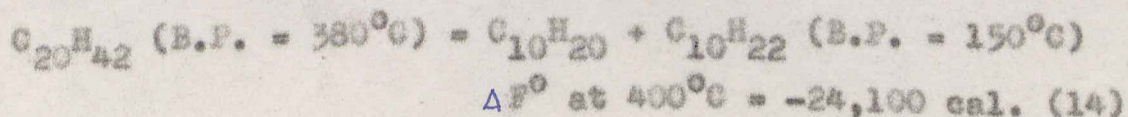
THE PYROLYSIS OF HYDROCARBON OILS

It has long been known that the oxides of many metals are effective in the decomposition of hydrocarbon oils. A patent in 1924 claims Fe_2O_3 as a cracking catalyst for heavy hydrocarbon oils at 550°C . (3) In 1931 activated alumina on a silica carrier was used in Germany to crack heavy hydrocarbons. In the Houdry process of cracking petroleum hydrocarbons, Al_2O_3 - SiO_2 catalysts have long been used. (7) In 1943 U.S. patent No. 2,288,874 was granted, claiming the conversion of hydrocarbons using siliceous materials modified with hydrochloric or sulfuric acid, as catalysts. Later, U.S. patents No. 2,495,751 (20), 2,330,685 (18), 2,398,825 (19), claimed conversion of hydrocarbons with clay catalysts activated by acid treatment, using HCl , H_2SO_4 and H_3PO_4 .

Since the treatment of Portland cement with acids gives a mixture of such oxides active in the pyrolysis of hydrocarbons, tests were made in this respect. Paraffin oil was found to be most adequate as a reagent to be cracked due to its purity and fairly uniform composition.

A. The Pyrolysis of Paraffin Oil.

Paraffin oil is a mixture of heavy, long chain, saturated hydrocarbons boiling at about 380°C . This corresponds to a saturated hydrocarbon with about 20 carbon atoms per chain. After pyrolysis it is found that the average boiling point of the paraffin oil which is cracked is about 150°C . This would correspond to a compound having about 10 carbon atoms in the chain. (6) The pyrolysis of paraffin oil may then be represented approximately by the equation



The percent cracking can be determined by dividing the

volume of oil which after catalysis boils lower than the original paraffin oil by the volume of the original oil used, and multiplying this quotient by one hundred. For instance, 50.0 cc of the original paraffin oil distil as follows:

<u>Boiling pt. range</u>	<u>Volume</u>
25 - 100°C	0 cc
100 - 200	0
200 - 300	0
300 - 350	5
350 - 400	45

After cracking, the 47 cc of oil recovered might distil something like this:

<u>Boiling pt. range</u>	<u>Volume</u>
25 - 100°C	10 cc
100 - 200	7
200 - 300	8
300 - 350	5
350 - 400	17

The first three figures indicate volumes boiling below the original boiling point, their sum adds up to 25 cc. Then the percent cracking for this particular run is $25/50 \times 100 = 50\%$.

The following are the percentages obtained by passing 50cc of paraffin oil over Catskill regular cement catalysts at 400°C and at a rate of 50 cc / 75 min., using the normal, vertical position of the catalyst tube:

TABLE X: The % Cracking for Various Catalysts

<u>Catalyst, Conc. of Acid</u>	<u>% Cracking</u>
Acetic acid, 16.0M	50%
12.0	48
6.0	46
4.0	32
3.0	16
Hydrochloric acid, 4.00M	10
2.70	14
2.65	16
2.45	12
2.35	12
2.25	25
2.15	12
2.00	6
Pyrex glass beads	0
U.O.P. Catalyst	56

Hydrogen is produced in most of these reactions, maxima being at 4.0M for the acetic acid gels (3.15 lit.), and at 2.25M for the hydrochloric acid gels (3.38 lit.). Only a few hundred cc of hydrogen are produced for the 16.0M and 12.0M RAc gels, where the percent cracking is highest.

Discussion of Results: The acetic acid gels show their usual trend: yields increase as the normality increases. Again, as in the case of the dehydration of ethyl alcohol, the percent yield increases rapidly with normality up to the normality of 6.0. From this point on up the yield increases only slightly. Thus yields increase 30% from 3.0M to 6.0M, but only 4% from 6.0M to 16.0M acetic acid. This would indicate that the same ingredients and the same structural and surface properties of the gels are responsible for the dehydration of alcohol and the pyrolysis of paraffin oil.

The hydrochloric acid cement gels show a maximum crac-

king capacity of 25% at the 2.25M acid concentration. In comparison with the acetic acid cement gels this is a rather low yield. The yield for the rest of the HCl gels is about 14%. In attempting to explain the maximum for the 2.25M gel, it should be noted that this is the first catalyst to have the CaO sufficiently removed to be up in the high yield range for the dehydration of ethyl alcohol. In addition, this gel has a maximum Al_2O_3 content, higher than that of any other HCl gel (see fig. 1). On the higher acid side the Al_2O_3 content drops off very rapidly, and on the lower acid side the CaO content becomes predominant. Since Al_2O_3 catalysts have long been used in the cracking industry, it is an active ingredient. Therefore this maximum Al_2O_3 content of the 2.25M HCl gel might serve as a possible explanation for its maximum cracking power.

To compare the cracking power of these cement gels to commercial catalysts, a Universal Oil Products Type "A" Fluid Cracking Catalyst was used with paraffin oil under identical conditions. The yield of 56% obtained with it is not greatly above the 50% obtained with the best of the acetic acid cement gels.

B. The Pyrolysis of Lubricating Oils

Three runs with heavy lubricating oils were made. Shell oils give 29 - 30% cracking, Sinclair oil 30%. Interpretation is difficult due to the complex composition of these oils.

ORGANIC COMPOUNDS UNAFFECTED BY CEMENT GEL CATALYSTS

The following compounds have been passed over various cement gel catalysts at 400°C at a rate of 50 cc per hour without being affected by this treatment:

n-heptane

aniline

phenol

acetic acid

benzene and ethyl alcohol: only ethylene produced.

chlorobenzene and ethyl alcohol: only ethylene
produced.

SUMMARY

Portland cement acid gels are excellent dehydrating catalysts in the vapor phase for methyl; ethyl; n-, iso-propyl; primary-, sec-, tert-butyl alcohol. Methyl alcohol dehydrates to the dimethyl ether, all other alcohols to their corresponding olefins. For ethyl alcohol yields of 90% of ethylene are obtained from the concentration of 6.0M acetic acid on up, and the concentration range between 2.25M and 2.70M hydrochloric acid.

In the dehydration of ethylene glycol to acetaldehyde the maxima exhibited are 50% for the 16.0M HAc gel, and 48% for the 2.70M HCl gel.

The most effective catalyst for the pyrolysis of paraffin oil is the 16.0M HAc Catskill regular cement gel which gives 50% cracking at a temperature of 400°C. 56% cracking is obtained with a commercial catalyst.

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